systems are of two sorts, viz., a point may lie on or off a line. We may therefore graphically represent such a system by using two sorts of graphical units, a pair of which, one of each sort, are either connected by a link or not, according as the point represented by one lies on the line represented by the other or not. The laws regulating the distribution of the links are stated, and the various forms which collections of three and four points and collections of three lines can assume are considered.
§§ 362-375. Collinear Points.

From the results of the sections under the preceding heading the form of a system of collinear points is deduced. It is shown to be a triadic group. The forms of tetrads of points of the system, both harmonic and anharmonic, are discussed.

> §§ 376-380. Ordinary Algebra.

From the preceding sections we naturally pass to the ordinary algebraic treatment of collinear points, and the nature of quantities.
§§ 381-387. Coplanar Points and Lines.
These admit of discussion as a double system. The distribution of the connecting pairs of the two systems is defined, and the algebraic treatment deduced.
§§ 388-389. Coplanar Points, Lines, and Conics.
These sections refer briefly to the nature of the treble system composed of coplanar points, lines, and conics.
§§ 390-426. Logic.
The memoir concludes with the consideration of the forms of systems of which the units are classes. The investigation leads to a recognition of the fact that on certain points a modification of the views held by modern logicians is necessary.
IV. "On the Influence of Temperature on the Heat of Dissolution of Salts in Water." By William A. Tilden, D Sc. Lond., F.R.S., Professor of Chemistry in the Mason Coliege, Birmingham. Received May 18, 1885.
The experiments described in this paper were undertaken in the hope of obtaining some light upon the vexed question of the condition in which a solid exists when dissolved in a liquid, and were directed more especially towards the investigation of the well-known remarkable phenomena exhibited by sodium sulphate.

Crystallised sodium sulphate melts at about $34^{\circ}$, and at this temperature the salt begins to show signs of dissociation by depositing the anhydrous compound. According to Wiedemann,* indeed, indications of change are observable at a few degrees lower. He finds by observation of the volume of the crystallised salt at different temperatures, that whereas slight expansion occurs from $17^{\circ}$ to about $30^{\circ}$, contraction then sets in, at first slowly, then, at $33^{\circ}$ to $34^{\circ}$, very rapidly, till the salt melts. The melted salt expands regularly in proportion as the temperature is raised to near $100^{\circ}$. Nicol $\dagger$ has made experiments upon the expansion of solutions of the same salt, and with similar results.

The solubility of sodium sulphate increases rapidly from ordinary temperatures up to $34^{\circ}$, when it attains a maximum. From this point upwards the solubility again diminishes very rapidly to between $40^{\circ}$ and $50^{\circ}$, and then less rapidly, till at $100^{\circ}$ to $160^{\circ}$ it becomes nearly stationary. At temperatures higher than $160^{\circ}$ the solubility slowly increases again. $\ddagger$

In 1874 it was observed by De Coppet§ that heat is developed by contact of water with anhydrous sodium sulphate at temperatures considerably above $34^{\circ}$, at which point the ordinary hydrate is broken up. This circumstance was attributed by Thomsen to the formation of a monohydrate, $\mathrm{Na}_{2} \mathrm{SO}_{4} \cdot \mathrm{H}_{2} \mathrm{O}$, and he ascribed this composition to the crystals which are deposited on heating a concentrated solution of sodium sulphate, and which had always been believed to be anhydrous. Thomsen's assumption has, however, been shown to be groundless, $\|$ and therefore the fact noticed by De Coppet remains without adequate explanation.

Below the temperature of $34^{\circ}$ it seems probable that the sodium sulphate dissolved in water is in the state of hydrate, $\mathrm{Na}_{2} \mathrm{SO}_{4} 10 \mathrm{H}_{2} \mathrm{O}$. In what condition is it at temperatures higher than $34^{\circ}$ ? In other words, does the solution contain the usual hydrate or the anhydrous salt, or both?

This is the question which I have endeavoured to attack by comparing the thermal changes attending the act of solution of the anhydrous salt in water at temperatures above this critical point with the corresponding change at temperatures below. Some interesting results have been obtained, but they do not supply a final answer to this question. My few earlier experiments, communicated in a short note to the British Association at Montreal, gave erroneous results, partly

[^0]because I was then unaware of the existence of the allotropic modifications of anhydrous sulphate of sodium since discovered by Mr. Pickering (loc. cit.), and partly from errors of experiments, which have sinco been corrected.

The apparatus I have used consists of two parts, the calorimeter and the constant temperature bath. The calorimeter is a brass drum 9 cm . high and 7 cm . diameter, having a paddle which works in a socket in the centre of the vessel, and the spindle of which passes through the lid. At the top of the spindle is a reel, round which passes a silk cord, the ends of which are weighted and drawn over pulleys placed at a little distance on opposite sides. By gently pulling' the cord at either end the paddle is made to spin round. Immediately above the blades of the paddle is a wide brass tube perforated with holes, and the bottom of which is immersed in the water, which is placed in the calorimeter. In this tube is placed a thin glass bulb containing the weighed quantity of salt and sealed at the blowpipe. Standing in the tube is a thin brass rod having a fork at the end to act as pulveriser, the top which projects through the lid of the calorimeter, being provided with a wooden handle. The thermometer stands in a perforated tube on the opposite side of the calorimeter. The cover of the calorimeter is provided with three holes, one for the stem of the thermometer, one in the centre for the paddle, and the third for the handle of the pulveriser. The vessel is supported on three sharp boxwood points within a covered brass case silvered inside, the space between the calorimeter and the case being about 1 cm . all round.

The bath employed for maintaining a constant temperature is practically identical with that described by Nicol,* but is provided with a well in the middle, into which fits closely the outer case of the calorimeter. The temperature of the water or oil is remarkably constant, and when the temperature does not exceed $30^{\circ}$ a thermometer in different parts of the bath does not vary by more than ${ }^{\circ} 05^{\circ}$. To assist in maintaining this constancy the bath is covered closely, and is enveloped in thick felt. Three thermometers were used-A, from $8^{\circ}$ to $26^{\circ} \mathrm{C}$., divided into twentieths; B, from $25^{\circ}$ to $50^{\circ}$, and C , from $42^{\circ}$ to $76^{\circ}$, both divided into tenths Centigrade, and the temperature could easily be read to $005^{\circ}$ and $\cdot 01^{\circ}$ respectively, or even half this.

The course of an experiment is as follows:-The water having been introduced into the calorimeter, and the thermometer inserted into its iube, the whole is placed in an oven until the thermometer indicates a temperature about half a degree above that to which the bath has been previously heated. The calorimeter is then put into the bath, the cover of the case is put on, and the thermometer read from time to time till the temperature is either quite stationary or is falling steadily at a rate which is recorded, and from which a correction can be intro-

$$
\text { * " Phil. Mag.," 1883, } 339 .
$$

duced into the observed result. The glass bulb is then broken, and the paddle gently worked by one person whilst another reads the thermometer by the telescope. In every case a definite interval (usually one or two minutes) is allowed to elapse before the final reading is taken, not only to allow time for solution, but for the alteration of temperature in the liquid to be imparted to the calorimeter. In those cases in which the calorimeter had been in the bath for some time at a rather high temperature, and there was reason to fear that slight loss had occurred by evaporation, the whole was weighed after the experiment was concluded, and a correction introduced accordingly. The amount thus lost never exceeded a gram or thereabouts, and as the thermal equivalent of the calorimeter and its contents amounted to 100 grams and upwards, the result is not appreciably affected.

In the accompanying tables the numbers contained in the column headed "Water equivalent of the calorimeter," include the values of the calorimeter, the glass bulb, the thermometer, and the solution, the specific heat of which is taken generally from Thomsen's numbers.

Three series of experiments were undertaken with sulphate of sodium, and the results are embodied in the three tables, $\mathrm{A}, \mathrm{B}$, and C.

For A the salt had been heated to redness, not to fusion, about a fortnight before.

For B the salt had been heated to redness one day before.
For C the precipitated salt had been dried at $120^{\circ}$.
These varieties were taken on account of the differences in the heat of dissolution of sulphate of sodium which have been observed by Mr. Pickering (lec. cit.).

Sodium Sulphate, $\mathrm{Na}_{2} \mathrm{SO}_{4}$, in 100 molecules of Water, or 142 parts in 1800 parts.

Weight of Salt used . . .. 6.311 grams.
Weight of Water used .. 80.000 ,
Specific heat of Solution $\mathrm{Na}_{2} \mathrm{SO}_{4} 100 \mathrm{H}_{2} \mathrm{O}=\cdot 927$.

| $\begin{aligned} & \text { Number } \\ & \text { of } \\ & \text { expt. } \end{aligned}$ | Water equiv. calorim., \&c. | Temperature. |  | Correction. | Total rise. | Molecular heat of dissolution. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | Before solution. | After solution. |  |  |  |
| Series A. |  |  |  |  |  |  |
| 1 | $110 \cdot 7$ | 33•46 | 34.00 | +.006 | -546 | 1360 |
| 2 | $110 \cdot 7$ | $33 \cdot 30$ | $33 \cdot 86$ | + $\cdot 010$ | -570 | 1419 |
| 3 | $110 \cdot 6$ | $33 \cdot 24$ | $33 \cdot 79$ | + $\cdot 005$ | -555 | 1381 |
| 4 | $110 \cdot 7$ | $34 \cdot 97$ | $35 \cdot 55$ | 0 | -580 | 1444 |
| 5 | $110 \cdot 6$ | $34 \cdot 90$ | $35 \cdot 49$ | 0 | -590 | 1468 |
| 6 | $110 \cdot 6$ | $35 \cdot 01$ | $35 \cdot 58$ | 0 | -570 | 1418 |
| 7 | $110 \cdot 7$ | $35 \cdot 41$ | $35 \cdot 93$ | + 010 | -530 | 1320 |
| 8 | $110 \cdot 7$ | $39 \cdot 70$ | $40 \cdot 30$ | 0 | -600 | 1494 |
| 9 | $110 \cdot 7$ | $39 \cdot 60$ | $40 \cdot 20$ | 0 | -600 | 1494 |
| 10 | $110 \cdot 7$ | $44 \cdot 07$ | $44 \cdot 68$ | -. 010 | $\cdot 600$ | 1494 |
| Series B. |  |  |  |  |  |  |
| 11 | $110 \cdot 7$ | $31 \cdot 19$ | $31 \cdot 70$ | 0 | - 510 | 1270 |
| 12 | $110 \cdot 6$ | $31 \cdot 50$ | $32 \cdot 01$ | 0 | . 510 | 1269 |
| 13 | $110 \cdot 7$ | $44 \cdot 28$ | $44 \cdot 98$ | - $\cdot 016$ | -684 | 1703 |
| 14 | $110 \cdot 7$ | $44 \cdot 755$ | $45 \cdot 490$ | 0 | $\cdot 735$ | 1830 |
| 15 | $110 \cdot 7$ | $44 \cdot 57$ | $45 \cdot 20$ | - 01 | -620 | 1544 |
| 16 | $110 \cdot 7$ | $45 \cdot 01$ | $45 \cdot 71$ | + 009 | -709 | 1766 |
| 17 | $110 \cdot 6$ | $63 \cdot 51$ | $64 \cdot 30$ | $+\cdot 022$ | -812 | 2020 |
| 18 | $110 \cdot 7$ | $67 \cdot 80$ | $68 \cdot 69$ | 0 | -890 | 2216 |
|  |  |  | SEries |  |  |  |
| 19 | $110 \cdot 7$ | $31 \cdot 60$ | $32 \cdot 06$ | 0 | -460 | 1146 |
| 20 | $110 \cdot 6$ | $31 \cdot 54$ | $32 \cdot 00$ | 0 | -460 | 1146 |
| 21. | $110 \cdot 7$ | $45 \cdot 00$ | 45.55 | 0 | -550 | 1369 |
| 22 | $110 \cdot 8$ | $44 \cdot 98$ | $45 \cdot 50$ | $+\cdot 006$ | -526 | 1311 |
| 23 | $110 \cdot 7$ | $60 \cdot 10$ | $60 \cdot 84$ | + $\cdot 01$ | $\cdot 750$ | 1869 |
| 24 | $110 \cdot 7$ | $64 \cdot 20$ | $64 \cdot 94$ | + 01 | $\cdot 750$ | 1869 |
| 25 | $110 \cdot 6$ | $64 \cdot 20$ | $64 \cdot 96$ | +.052 | -812 | 2020 |

Mean Results.

| No. in table. | Temp. approx. | Heat of dissolution. |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | A. | B. | C. |
| 11, 12 | $31^{\circ}$ | - | 1270 |  |
| 19, 20 | 32 | $\ddot{\square}$ | .. | 1146 |
| 1, 2, 3 | 33 | 1387 |  |  |
| 4, 5, 6, 7 | 35 | 1412 |  |  |
| 8,9 | 40 | 1494 |  |  |
| $10 \mathrm{~A}, 13 \mathrm{~B}$ | 44 | 1494 | 1703 |  |
| 14, 15, 168, 21, 22c | 45 | . | 1713 | 1340 |
| 23 23 | 60 | . |  | 1869 |
| $17 \mathrm{~B}, 24,25 \mathrm{c}$ | 64 68 | $\cdots$ | 2020 2216 | 1945 |
| 18 | 68 | -• | 2216 |  |

From these figures it appears that although the manner in which the salt has been prepared influences the result very notably, yet in each series, comparing together the effects of dissolving the same kind of anhydrous sodium sulphate, the heat of dissolution increases progressively with rise of temperature. That this would be the case might be predicted by applying the principle originally indicated by Person,* and since discussed by Berthelot $\dagger$ and by Thomsen, $\ddagger$ and embodied in the general equation $Q_{T}=Q_{t}+U-V$, where $Q_{T}$ and $Q_{t}$ are the quantities of heat evolved in the act of solution at the temperatures $\mathrm{T}^{\circ}$ and $t^{\circ}$, and U represents the sum of the capacities for heat of the salt and the water, and $V$ represents the capacity of the solution between the temperatures $\mathrm{T}^{\circ}$ and $t^{\circ}$.

The salt A must be regarded as being in the most stable condition of the three, and the following comparison of the numerical values of the thermal change observed and calculated, applies to the A series of experiments:-

$$
\mathrm{U}=(18 n+\mathrm{C})(\mathrm{T}-t) .
$$

$n$ is the number of water molecules.
C is the molecular heat of the salt.
$\mathrm{V}=(18 n+\mathrm{K})(\mathrm{T}-t)$.
$\mathrm{C}=32 \cdot 2$ (Kopp).
$18 n+\mathrm{K}=1815$ (Marignac).
Take $\mathrm{Q}_{t}$ at $34^{\circ}=1400$, which is the mean of numbers given above for $33^{\circ}$ and $35^{\circ}$,

Then $Q_{T}=1503$ when $T=40^{\circ}$.

$$
=1537 \text { when } T=42^{\circ} .
$$

$$
=1572 \text { when } \mathrm{T}=44^{\circ} .
$$

From $40^{\circ}$ to $44^{\circ}$ observed 1494.
There is not much difference here, but the observed is less than the calculated number.

Carbonate of sodium was next examined on account of its close resemblance to sulphate of sodium in water of crystallisation, melting point, and solubility.

Sodium Carbonate, $\mathrm{Na}_{2} \mathrm{CO}_{3}$, in 100 molecules of Water, or 106 parts in 1800 parts by weight.

$$
\begin{aligned}
& \text { Weight of Salt used .. } \quad \text {. } 5.005 \text { grams. } \\
& \text { Weight of Water used.. } \quad \text {.. } 85.0 \quad "
\end{aligned}
$$

Specific Heat of Solution $\mathrm{Na}_{2} \mathrm{CO}_{3} \cdot 100 \mathrm{H}_{2} \mathrm{O}=\cdot 933$.

| Number of expt. | Water equiv. calorim., $\& c$. | Temperature. |  | Correction. | Total rise. | Molecular heat of dissolution. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | Before solution. | After solution. |  |  |  |
| 26 | $116 \cdot 2$ | 21.85 | $24 \cdot 37$ | + 075 | $2 \cdot 595$ | 6388 |
| 27 | $116 \cdot 3$ | $21 \cdot 80$ | $24 \cdot 25$ | + $\cdot 058$ | $2 \cdot 508$ | 6177 |
| 28 | $117 \cdot 5$ | $22 \cdot 545$ | $25 \cdot 050$ | + $\cdot 1075$ | $2 \cdot 6125$ | 6485 |
| 29 | $117 \cdot 4$ | $22 \cdot 39$ | $24 \cdot 82$ | + 079 | $2 \cdot 509$ | 6238 |
| 30 | 116.2 | $35 \cdot 60$ | $38 \cdot 40$ | 0 | $2 \cdot 800$ | 6887 |
| 31 | $116 \cdot 2$ | $35 \cdot 28$ | 38.08 | 0 | $2 \cdot 800$ | 6887 |
| 32 | $116 \cdot 2$ | $35 \cdot 70$ | 38.50 | 0 | $2 \cdot 800$ | 6887 |
| 33 | $116 \cdot 3$ | $38 \cdot 18$ | $40 \cdot 90$ | + $\cdot 004$ | $2 \cdot 724$ | 6708 |
| 34 | $116 \cdot 3$ | $38 \cdot 97$ | $41 \cdot 60$ | + 112 | $2 \cdot 742$ | 6753 |
| 35 | $116 \cdot 1$ | $43 \cdot 55$ | $46 \cdot 30$ | + 015 | $2 \cdot 765$ | 6785 |
| 36 | $116 \cdot 3$ | $50 \cdot 40$ | $53 \cdot 16$ | + 020 | $2 \cdot 780$ | 6846 |
| 37 | $115 \cdot 1$ | $55 \cdot 25$ | 58.08 | 0 | $2 \cdot 790$ | 6783 |
| 38 | $114 \cdot 9$ | $54 \cdot 73$ | $57 \cdot 58$ | 0 | $2 \cdot 850$ | 6923 |
| 39 | $116 \cdot 1$ | $54 \cdot 60$ | $57 \cdot 50$ | - 0002 | $2 \cdot 898$ | 7128 |
| 40 | $116 \cdot 2$ | $54 \cdot 30$ | $57 \cdot 18$ | 0 | $2 \cdot 880$ | 7067 |
| 41 | $115 \cdot 1$ | $56 \cdot 00$ | $58 \cdot 875$ | 0 | $2 \cdot 875$ | 7004 |

The carbonate of sodium used in these experiments had been heated to redness, but at times which varied from a few hours to several days before the experiment. Some of the irregularities in the numbers may be not improbably due to this circumstance. But the mean results show on the whole an increase in the heat of dissolution with rise of temperature.

| Experiment number. | Approximate temperature. | Mean heat of dissolution. |
| :---: | :---: | :---: |
| 26 to 29 | $22^{\circ}$ | 6322 |
| 30 ,, 33 | $35-40^{\circ}$ | 6842 |
| $34, \ldots 35$ | $40-45^{\circ}$ | 6769 |
| 36,41 | $50-55^{\circ}$ | 6958 |

Calculated from the figure for $22^{\circ}=6322$, taking $\mathrm{C}=26 \cdot 1$ (Kopp), $18 n+\mathrm{K}=1778$ (Thomsen), $\mathrm{T}=55^{\circ}$.
$\mathrm{Q}_{\mathrm{T}}=7909$, which is much higher than 7128 , the greatest observed value at $55-56^{\circ}$.

For the sake of comparison sulphate of potassium, which always crystallises without water, was taken with the following resultis:-

Potassium Sulphate, $\mathrm{K}_{2} \mathrm{SO}_{4}$, in 100 molecules of Water, or 174 parts in 1800 parts by weight.

$$
\begin{array}{llll}
\text { Weight of Salt used .. } & \text {.. } & 7 \cdot 733 \text { grams. } \\
\text { Weight of Water used.. } & . . & 80 \cdot 00
\end{array}
$$

Specific Heat of Solution $\mathrm{K}_{2} \mathrm{SO}_{4} \cdot 100 \mathrm{H}_{2} \mathrm{O}=\cdot 8965$.


Take $Q_{t}$ at $15^{\circ}=-5338$.
$\mathbf{C}=34 \cdot 1$ (Kopp) and $18 n+\mathrm{K}=1781$ (Marignac).
$\mathrm{T}=45^{\circ}$.
$\mathrm{Q}_{\mathrm{T}}=-3745$. Observed -4730. Difference, 985.

In the solution of anhydrous carbonate and sulphate of sodium in water, evolution of heat occurs, and the amount of heat evolved increases with the temperature, but is not so great as would be inferred from the application of Person's formula. On the other hand, sulphate of potassium, the solution of which is attended by absorption of heat, gives a gradually diminishing absorption as the temperature is raised, but the observed absorption is greater at the higher temperature thau the calculated amount. That is to say, in all these cases, whether the act of solution is attended by rise or fall of temperature, there is a consumption of energy corresponding to an absorption of beat, which is not accounted for by the difference between the specific heats of the materials, and of the solution which results from their union.

From the connexion already established between fusibility and solubility,* and from à priori considerations, it seemed probable that the thermal change attending the solution of a solid must vary according as by raising the temperature the cohesion of the solid is diminished, or by lowering the temperature the cohesion is increased. For if a salt dissolves in water with absorption of heat, this absorption will be less at higher temperatures when the cohesion of the solid has been reduced, and therefore the energy required for its liquefaction by the solvent also lessened. On the other hand, if a salt dissolves with evolution of heat, the heat evolved must be greater at higher temperatures for the same reason.

Some very fusible salts were therefore taken in order to ascertain whether the difference between the observed and calculated heats of solution was notably greater or less than the difference observed in the case of the sodium carbonate and sulphate and potassium sulphates.

[^1]Potassium Nitrate, $\mathrm{KNO}_{3}$, in 100 molecules of Water, or $101 \cdot 1$ parts in 1800 parts by weight.

| Weight of Salt used .. | .. | $4 \cdot 774$ grams. |
| :--- | :--- | :--- | :--- |
| Weight of Water used.. | .. | $85 \quad$, |

Specific Heat of Solution $\mathrm{KNO}_{3} 100 \mathrm{H}_{2} \mathrm{O}=\cdot 942$.

| Number <br> of <br> expt. | Water <br> equiv. <br> calorim., <br> \&c. | Temperature. <br> Before <br> solution. |  | After <br> solution. | Correction. | Total <br> fall. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Molecular <br> heat of <br> dissolution. |  |  |  |  |  |
|  |  |  |  |  |  |  |
| 54 | $116 \cdot 8$ | $15 \cdot 55$ | $12 \cdot 30$ | 0 | $3 \cdot 25$ | 8028 |
| 55 | $116 \cdot 7$ | $15 \cdot 50$ | $12 \cdot 30$ | 0 | $3 \cdot 20$ | 7906 |
| 56 | $116 \cdot 7$ | $34 \cdot 42$ | $31 \cdot 30$ | 0 | $3 \cdot 12$ | 7703 |
| 57 | $116 \cdot 7$ | $34 \cdot 61$ | $31 \cdot 39$ | $-\cdot 006$ | $3 \cdot 214$ | 7926 |
| 58 | $116 \cdot 7$ | $52 \cdot 72$ | $49 \cdot 60$ | $-\cdot 015$ | $3 \cdot 105$ | 7662 |
| 59 | $116 \cdot 7$ | $53 \cdot 88$ | $50 \cdot 87$ | -.004 | $3 \cdot 006$ | 7421 |

Mean.

| Approximate <br> temperature. |  | Heat of <br> $15^{\circ}$ <br> dissolution. |
| :---: | :---: | :---: |
| 34 | $\ldots \ldots \ldots \ldots \ldots$ | -7967 |
| 53 | $\ldots \ldots \ldots \ldots \ldots$ | -7814 |
|  | $\ldots \ldots \ldots \ldots$ | -7541 |

From the values $\mathrm{C}=23 \cdot 2$ (Kopp), $18 n+\mathrm{K}=1791$ (Thomsen), and $\mathrm{Q}_{t}=-7967$ at $15^{\circ}, \mathrm{Q}_{\mathrm{T}}=-6751$ when $\mathrm{T}=53^{\circ}$.

Sodium Nitrate, $\mathrm{NaNO}_{3}$, in 100 molecules of Water, or 85 parts in 1830 parts by weight.

$$
\begin{array}{llll}
\text { Weight of Salt used .. } & \text {.. } & 4 \cdot 013 \text { grams. } \\
\text { Weight of Water used .. } & \text {.. } 85 \cdot 0 \quad "
\end{array}
$$

Specific Heat of Solution $\mathrm{NaNO}_{3} \cdot 100 \mathrm{H}_{2} \mathrm{O}=950$.

| Number <br> of <br> expt. | Water <br> equiv. <br> calorim., <br> \&c. | Temperature. <br> Before <br> solution. |  | After <br> solution. | Correction. | Total <br> fall. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | Molecular <br> heat of <br> dissolution. |  |  |  |  |
|  | $116 \cdot 8$ | $16 \cdot 30$ | $14 \cdot 36$ | $-\cdot 003$ | $1 \cdot 937$ | 4776 |
| 61 | $116 \cdot 8$ | $16 \cdot 05$ | $14 \cdot 15$ | $+\cdot 040$ | $1 \cdot 940$ | 4796 |
| 62 | $116 \cdot 8$ | $54 \cdot 42$ | $52 \cdot 67$ | $-\cdot 004$ | $1 \cdot 746$ | 4306 |
| 63 | $116 \cdot 8$ | $54 \cdot 80$ | $53 \cdot 09$ | $-\cdot 002$ | $1 \cdot 708$ | 4204 |

Mean.
Heat of
dissolution.
Temperature.
$16^{\circ}$
$-4786$
54 ................ -4255

Calculated from the values $\mathrm{C}=21.8$ (Kopp), $18 n \mathrm{~K}=1791$ (Thomsen), and taking $\mathrm{Q}_{t}=-4786$ at $16^{\circ}, \mathrm{Q}_{\mathrm{T}}=-3616$ when T is $54^{\circ}$.

The observed and calculated numbers for potassium sulphate and. nitrate and sodium nitrate are plotted out in the diagram below, where it is manifest that there is a difference between the two nitrates and the much less fusible and soluble sulphate. For tracing up the abscissa for $45^{\circ}$, we see that the difference between the observed and calculated numbers for potassium sulphate amounts to upwards of 900 calories, whilst the corresponding difference in nitrate of sodium is only about 500, and in nitrate of potassium about 700.


Experiments published in 1873 by Winkelmann,* on the solution of the potassium, sodium, and ammoniam chlorides and nitrates in water at different temperatures lead to similar conclusions. Thus taking Winkelmann's figure representing the heat of dissolution of nitrate of sodium, 1 gram of salt in 20.80 grams of water, which is very nearly 1 mol . of salt to 100 mols . of water-

$$
\begin{aligned}
& \text { At } 2-3^{\circ} \text { gives as a mean }-60 \cdot 30 \text { cal. } \\
& \text { At } 50-51^{\circ} ", ", \quad, 48 \cdot 70,
\end{aligned}
$$

For a molecule of salt, or 85 grams-

$$
\begin{aligned}
& 60 \cdot 3 \times 85=5125 \cdot 5 \\
& 48 \cdot 7 \times 85=4139 \cdot 5 .
\end{aligned}
$$

By the formula-

$$
Q_{\mathrm{T}}=\mathrm{Q}_{t}+[(18 n+\mathrm{C})-(18 n+\mathrm{K})](\mathrm{T}-t),
$$

and using the values already given for sodium nitrate,

$$
Q_{T}=-3646 \cdot 6,
$$

and this is very nearly identical with the number calculated from my own experiment at $16^{\circ}$.

I have made a few determinations of heat of solution of the crystallised sulphate and carbonate of sodium. Whilst these salts dissolve at common temperatures, with great absorption of heat, the absorption at the melting point is very feeble, and at a few degrees higher is changed into evolution of heat. This last-named effect is probably due to the fact that when heated beyond their melting point, $34^{\circ}$ (circa), these salts are partly deposited in a solid dehydrated state.

[^2]Sodium Sulphate, $\mathrm{Na}_{2} \mathrm{SO}_{4} 10 \mathrm{H}_{2} \mathrm{O}$ in 190 molecules of Water, or 322 parts by weight in 3420 parts of Water.

$$
\begin{aligned}
& \text { Weight of Salt used .. .. } 8 \cdot 05 \text { grams. } \\
& \text { Weight of Water used.. } \quad . .85 \cdot 5
\end{aligned}
$$

Specific Heat of Solution $\mathrm{Na}_{2} \mathrm{SO}_{4} \cdot 200 \mathrm{H}_{2} \mathrm{O}=955$.

| Water equiv. calorim., \& c . | Temperature. |  | Correction. | Total change. | Molecular heat of dissolution. | Mean. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Before solution. | After solution. |  |  |  |  |
| $121 \cdot 4$ | $16 \cdot 390$ | $12 \cdot 945$ | + 255 | $-3 \cdot 700$ | -17939 | -18035 |
| $121 \cdot 1$ | $16 \cdot 250$ | $12 \cdot 800$ | + 300 | -3.750 | -18131 | $-18035$ |
| $121 \cdot 4$ | $34 \cdot 180$ | $34 \cdot 040$ | - $0: 14$ | $-0 \cdot 136$ | - 660 | - 660 |
| $121 \cdot 3$ | $48 \cdot 150$ | $48 \cdot 200$ | - $\cdot 004$ | + $0 \cdot 046$ | + 223 | + 223 |

Sodium Carbonate, $\mathrm{Na}_{2} \mathrm{CO}_{3} \cdot 10 \mathrm{H}_{2} \mathrm{O}$, in 180 molecules, or 286 parts in 3240 parts by weight of Water.

| Weight of Salt used .. |
| :--- |
| Weight of Water used.. |

Specific Heat of Solution $\mathrm{NaCO}_{3} \cdot 190 \mathrm{H}_{2} \mathrm{O}=950$ approximately.

| Water equiv. calorim., $\& c$. | Temperature. |  | Correction. | Total change. | Molecular heat of dissolution. | Mean. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Before solution | After solution. |  |  |  |  |
| $117 \cdot 3$ | $15 \cdot 025$ | $12 \cdot 020$ | + 1312 | $-3 \cdot 1362$ | -14714 | -14714 |
| $116 \cdot 1$ | $34 \cdot 820$ | $34 \cdot 500$ | - 01014 | -306 | - 1405 $\}$ |  |
| $116 \cdot 1$ | $34 \cdot 300$ | $34 \cdot 050$ | +.005 | $\cdot 255$ | $-1171\}$ | - 1288 |
| $116 \cdot 1$ | $39 \cdot 390$ | $39 \cdot 300$ | + $\cdot 0075$ | -0975 | - 446 | - 446 |
| $116 \cdot 1$ | $47 \cdot 710$ | $47 \cdot 690$ | 0 | -020 | - 91 | - 91 |
| $116 \cdot 1$ | $48 \cdot 040$ | $48 \cdot 100$ | 0 | +0.062 | $+275\}$ | + 311 |
| $116 \cdot 1$ | $48 \cdot 230$ | $48 \cdot 300$ | - $\cdot 005$ | $\cdot 075$ | $+347\}$ | + 311 |

The very rapid decline in the heat absorption attending the solution of these two salts cannot be accounted for by Person's principle, whatever value be considered probable for the specific heat of the solid salt.

The process of dissolving a solid in a liquid must be considered as involving several distinct operations. Person seems to have been the first to point out that the change of state from solid to liquid must

[^3]be distinguished from the intermixture of the liquefied solid with the water. Both these acts must be attended by heat-absorption. The dilution of watery solutions has been shown, especially by the researches of Thomsen, to be attended very generally by absorption of heat, notwithstanding that in most cases it is accompanied by contraction of volume, a process which must have an opposite effect.

In the solution of many anhydrous and even hydrated salts, we must believe, from the very energetic thermal change observed, that the salt enters into chemical union with a portion of the liquid. The extent to which this combination occurs will be greatly influenced by the temperature at which the experiment is made, and at sufficiently elevated temperatures it must be believed to be entirely annulled, whilst on the other hand, as the temperature is raised, chemical action, resulting in double decomposition between the water and constituents of the salt, becomes apparent. This action, which is manifested in the case of the salts of the heavy metals by the production of insoluble oxides, hydroxides, or basic salts, cannot be supposed to be altogether without effect in the case of the salts of the alkali metals such as I have been examining, and I incline strongly to the belief that a part of the difference which I have pointed out between the observed heat of solution and the same calculated according to Person's formula, is due to this decomposing action of the water.

It is manifest that no theory of solution can be accepted which does not take cognisance of all these facts.

In conclusion, I desire to acknowledge the intelligent assistance I have received in the conduct of these experiments from Mr. Harold P. White.
> V. "On Radiant Matter Spectroscopy. Part II. Samarium." By William Crookes, F.R.S. Received May 21, 1885.

(Abstract.)
In the concluding sentence of the Bakerian Lecture which I had the honour to deliver before the Royal Society, May 31st, 1883, I said that the new method of Radiant Matter Spectroscopy there described had not only given me spectrum indications of the presence of yttrium as an almost invariable, though very minute, constituent of a large number of minerals, but had likewise revealed signs of another spectrum-yielding element. I stated that I had repeatedly seen indications of another very beautiful spectrum characterised by a strong red and a double orange band.



[^0]:    * " Pogg. Ann.," 1882, 561.
    + "Ber. Deut. Chem. Ges.," xv, 1931 b.
    $\ddagger$ Tilden and Shenstone, "Phil. Trans.," 1884, I, 23.
    § "Comp. Rend.," 79, 167.
    || De Coppet, " Ber. Deut. Chem. Ges.," xii, 248, and Pickering, "Jour. Chem. Soc.," 1884, 689.

[^1]:    * Carnelley, "Phil. Mag.," March, 1882 Tilden ; and Shenstone, " Phil. Trans.," 1884, I ; Tilden, "J. Chem. Soc.," July, 1884.

[^2]:    * "Pogg. Annalen," cxlix, 1. Winkelmann s experiments were directed towards the object of determining the specific heat of the solutions of these six salts. One difficulty in the way of the general application of this method is the uncertainty attaching to the specific heats of the salts in the solid state, by reason of the variability of their properties according to the manner in which they have been prepared.

[^3]:    * Thomsen's figure at $18^{\circ}$ is -18509 .

